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## BIOCHEMICAL NATURE OF GLEY FORMATION DURING AGING OF CLAYEY MATERIALS (REVIEW)

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The biochemical nature of gley formation during aging of clayey materials (CMs), the factors under which the process arises, methods of identification, and its effect on the properties of CMs are examined. It is shown that necessary factors are the moisture content of CMs and the content of organic matter and natural microflora as well as maintaining the optimal temperature during the aging period. A comprehensive assessment using color characteristics, the redox state of the medium, and chemical criteria based on the ratio of the forms of iron compounds, is proposed for identifying the biochemical processes and determining the optimal aging time of CMs.

**Key words:** clayey material, biochemical processes, gley formation, color characteristics, reduction of iron, redox potential.

The differences in the properties of clayey materials (CMs) are explained by their genesis, weathering conditions, and their technological preparation, including an aging stage on open sites or in special enclosures (storehouse, cellar, and so forth). The weathering and aging of CMs consist of a series of elementary stages, among which physical (aggregation, dispersion, and swelling), chemical (hydrolysis, hydration, oxidation-reduction, and others), and biochemical, due to the action of microflora and its metabolites, stages stand out.

The aging process is accompanied by a change of the color of CMs from red-brown (in the direction of cold tones) to grey, grey-light-blue, or grey-green, indicating the occurrence of similar soil gleying processes [2]. The gley-formation process has been scientifically substantiated and described in detail [3]. But only the general features of this process have been indicated in order to understand the essence and mechanism of the changes enumerated above, which are observed during aging of CMs and ceramic pastes [4, 5].

The present article examines the biochemical nature of the gley formation process occurring during aging, the factors under which this process appears, methods of identifying it, and its effect on the properties of CMs and ceramics based on them.

It is well known that the pattern of the color change of CMs which contain clays, kaolins or porcelain stones and their properties and conditions of weathering or aging have been used in the ceramic technology for a long time. The first

attempts to use color as a means for grading clays with respect to quality were described in 1737–1740 in a treatise-codex, which is called “Duties of an Architectural Expedition,” where it is indicated that clays used for bricks are divided “generally into four types: white, red, and blue” [6]. It is noted that blue clay is more plastic and brick based on such clay is stronger and harder.

In [4, 7, 8] color was chosen as the indicator of biochemical processes occurring in CMs. The color change is regarded as an indicator due to the transformation of compounds of iron, as a typomorphic chemical element, due to the creation of definite conditions.

The most important biochemical processes occurring in CMs during weathering and aging are described below (see Table 1) [8].

**Rubefaction** — biochemical process occurring during dehydration in an oxidative state and promoting the formation of hematite, when its fraction among the iron compounds is high.

**Browning** — biochemical process with oxidative conditions predominating for the formation of Fe(III) particles — hydroxides and oxides with decreasing fraction of hematite — by two mechanisms: destructive, associated with a decrease of the hematite fraction with relative accumulation of goethite as a result of moderate waterlogging, and synthetic, due to goethitization of the surface of hematite and feroxite particles, as well as crystallization of goethite with decomposition of adsorption organic iron complexes (biogenic mechanism).

**Gleying** — biochemical and biological processes occurring in the reduced state of CMs with stagnant or stagnat-

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**TABLE 1.**

Process	Material color	Moisture content and water regime	Oxidation-reduction state	Microbiological processes
Rubefaction	Dark-red, orange-red	$W_m \rightarrow 0$	Oxidized	Aerobic
Browning	Brown	$W_m \rightarrow 0$	"	"
Gleying	Blue-green Grey-light-blue	$W_m \rightarrow 0$ (stagnant) Same	Reduced "	Anaerobic "
Olivization	Olive (with the minerals illite or smectite present in the composition)	Temporary waterlogging	Oxidized, reduced, oxidized	Aerobic, anaerobic, aerobic

laving water regimes. The predominant colors of gleyed CMs are blue-green or grey-light-blue. Depending on the character of the transformation of the iron compounds, gleys are divided into two types: iron-free, predominantly in the laving moisture regime (grey-light-blue color of CMs), and reduced, which incorporates the formation of Fe(II) compounds, mainly in the stagnant regime (blue-green color).

**Olivization** — a result of the combined effect of alternating reduction and oxidation processes associated with temporary waterlogging. The olivization mechanism is absorption of iron from the composition of the hydroxide films by an octahedral layer of layered silicates (smectites and illites) in the form of  $\text{Fe}^{2+}$  ions in a reducing medium of waterlogged CMs. After CMs are aerated the iron is fixed as  $\text{Fe}^{3+}$  in their lattice, and the CMs acquire a yellow-green, olive color. In this process in CMs, iron is mainly redistributed between two forms: free hydroxide iron and iron in the layered-silicate lattice.

The color indicators of gleying under the conditions of stagnant water at 18 – 30°C are already seen after an aging time of 7 days. The intensity of gleying is closely related with the duration of waterlogging and with the concentration of the organic material [9]. However, the color of the gley is very unstable and on contact with oxygen it transforms, depending on the mineral composition of the CMs, the type of water regime, temperature composition, and the conditions of oxygenesis.

**Factors for the Appearance of Gleying of CMs.** The necessary and sufficient factors for gleying to occur include the following: the moisture content of CMs and the content of organic matter as well as natural microflora.

The temperature regime of the surrounding medium together with the direct effect on the redox potential (ORP) largely acts on it indirectly, intensifying or decreasing the activity of biochemical processes. Maximum and minimum values and an optimum, for which growth of microorganisms or their other functions are at a maximum level, are established for each group of microorganisms. For example, the optimum temperature for mesophylls is 20 – 25°C, and the maximum temperature is 45°C, which is close to the maximum solar heating of the rock [10]. Near the optimal temperature the microbiological activity of the mesophylls increases, and this is accompanied by an increase of oxygen

absorption and accumulation of the products of their activity — reduced compounds.

*First important condition* — the moisture content is considered to be the main factor limiting structure formation during aging of CMs. Depending on the moisture content a disperse system of CMs transforms into a plastic or fluid state; the rheological, textural, and other parameters of the system change. As a result of the increase of the moisture content of the CMs, the microbiological factor starts to play the leading role in the formation of their microstructure: aeration and depletion of the oxygen stores occurs very rapidly — in 1 – 2 days — in the bulk of the mass; this is accompanied by a drop of the ORP and transformation of an entire series of compounds of mineral and organic nature; the ratio between the aerobic and anaerobic micro-organisms changes in the direction of anaerobic predominance [4, 5, 7].

The period of waterlogging should be viewed as a short-time or prolonged phase in which the water regime must be taken into account: stagnant or stagnant-laving. Standing out among the complex of factors associated with gleying of CMs is the periodic change of the water regime (stagnant-laving), change of the waterlogging regime to a dehydration and desiccation regime and cyclic change of the redox state associated with this. This type of regime is characteristic for aging of CMs on open sites, in special volumes or directly in the pit after the overburden has been removed.

The biochemical state of the CM mass fundamentally changes when a stagnant regime appears: finely dispersed minerals and organic mineral compounds, which are CM constituents, insoluble under oxidative conditions, transform under reducing conditions into soluble, mobile, reactive forms. The stagnant-laving regime is characterized by the fact that a liquid phase fills all pores of the initial rock, creating the conditions for anaerobiosis, and then seeps through the volume used, carrying the products of interaction out of the reaction region.

*Second condition* — the presence of organic matter. Gley formation does not occur without the participation of organic matter. Two cases where aging of CMs occurs must be taken into account. In the first place, it can occur under conditions where the CMs do not contain organic matter capable of fermenting. In this case water logging is accompanied by hydration and moisture swelling of mineral colloids. It is significant that under such conditions a CM can remain in the

waterlogged state indefinitely without anaerobic conditions appearing, and the solid phase does not change much. In the second place, waterlogging can occur in the presence of organic matter capable of fermenting. In this case the aging of CMs is accompanied by processes that are characteristic for gley formation: lowering of the ORP, accumulation of organic and mineral reducing agents, acids and complex compounds, reduction and migration of iron.

Organic matter is one of the most important regulators of the aging process in CMs that are associated with oxidation-reduction conditions. Organic matter plays three roles. In the first place, it is a source of energy and nourishment, supporting the vital activity of microbic cenosis and thereby determining the intensity and direction of the oxidation-reduction processes in CMs. In the second place, organic matter or, more accurately, the products of vital activity at different trophic levels participate in the oxidation-reduction reactions and purely chemically, possessing a quite strongly expressed reducing power. In the third place, the organic materials themselves change the redox state of CMs under the action of biochemical and chemical processes, especially for redox potentials  $Eh$  to 200 – 100 mV and below, and they are transformed in different directions with compounds having a number of special characteristics being formed. Their hydrophilicity is strongly expressed, which, in turn, promotes the growth of moisture swelling; a number of compounds act as surfactants capable of disaggregating clayey particles and lowering the filtration power of the suspension.

According to D. Lovley's scheme [11] organic matter forms two groups with respect to composition and participation in the Fe(III) reduction:

organic matter as a source of energy (lactate, lactic acid, sugar), i.e., as a supplier of electrons; it is not oxidized in the process;

organic matter as an electron shuttle transporting electrons from iron-reducing bacteria to Fe(II).

An insufficiency of group of organic compounds can stop the reduction of Fe(III). Compounds capable of participating in reversible redox reactions can act as electron shuttles. An electron-shuttle molecule is reduced by a microorganism acting as a terminal electron acceptor and then transports the electrons to iron hydroxide, reducing it, and once again becomes oxidized. On account of the electron shuttle the reducing bacteria do not need to come into direct contact with iron hydroxides. In contrast to organic matter of the first group, an electron shuttle is not consumed in the Fe(III) reduction process. It is evident that to model gleying it is necessary to introduce, aside from a source of energy — sugar, compounds to improve electron transport in order to accelerate the process.

*Third condition* — the presence of microorganisms in CMs. One direction for developing methods of using microorganism to destroy silicates, enriching the mineral raw materials and improving the properties of ceramic masses, uses the so-called group of silicate bacteria, which were identified and described by V. G. Aleksandrov and coworkers [12].

K. I. Surman was the first to indicate that V. G. Aleksandrov's ideas about the presence of silicate bacteria were not adequately substantiated [13]; Surman obtained experimental proof of the fact that *B. mucilaginosus* — an ordinary soil heterotrophic bacillus — is incapable of growing without organic compounds. Subsequently, these data were confirmed in more detailed studies of the various strains of *B. mucilaginosus* in the works of Z. A. Avakyan, T. A. Pivovarova, and G. I. Garavaiko [14].

First, attempts were made to increase the effectiveness of aging by introducing simultaneously pure cultures of microorganisms and a nutrient medium into CMs [15, 16]. An advantage of this method is that during the period of preparation and development of the colony of bacteria of the culture *B. mucilaginosus* they form exopolysaccharides — metabolites of the vital activity of these bacteria, which act as surfactants and participate in the destruction of aggregates of clayey particles. But this method is labor-intensive and expensive and its results are not guaranteed: the metabolism of the strains of bacteria removed from and introduced into CMs slows down as the nutrient is consumed and then stops completely. In this case the microorganisms which are introduced compete with the natural forms of CMs. Correspondingly the forms which are best adapted to these conditions are selected. When a single substrate is used the gain is found to be due to the forms whose characteristics permit the best multiplication and survival under the given conditions. As a rule, natural microflora wins the competition for food.

This has led to a second direction of microbiological methods — use of natural microflora of CMs [4, 5, 9]. Studies of the propagation of microorganisms in the samples of clay, kaolin, and porcelain stone have shown that microflora, including heterotrophic bacteria, bacteria that perform fermentation, and denitrifying, sulfate- and iron-reducing bacteria, are present in all samples [7].

M. Hochella has examined the processes of synthesis, decomposition, transformation, and recrystallization of many minerals resulting from the vital activity of various microorganisms have been examined in the review [17]. One factor accelerating the transformation of CMs (destruction of macro- and microaggregates, decomposition and dissolution of minerals, and so forth) is the oxidation-reduction state and acidity of their medium. As a result of metabolizing matter microorganisms release into the medium various metabolites which are strong chemical reagents. Therefore, by shifting the parameters pH and  $Eh$  microorganisms can indirectly act on aging processes in CMs. But there is a difference between the biogenic phenomena and phenomena of a purely chemical nature, in which the role of the biogenic component is not limited to changing the chemical characteristics, first and foremost, the pH and  $Eh$  of the CM medium. It is known [18, 19] that the rate of decomposition of a number of silicates by certain microorganisms or their metabolites (biogenic path) is many-fold higher than under the action of any inorganic solvents with a concentration that is realistic for objects in nature (abiogenic path). Therefore, organic matter

participates in practically all gley-genesis processes but the kinetics of biogenic decomposition of the main minerals differs radically from the abiogenic kinetics: mechanisms, rates and intermediate products of reduction.

A natural community of microorganisms acts as a metabolic entity, uniting organisms with different trophic functions [10]. The interacting microorganisms are intercoupled either by competing for substrates which they use in common (nutrient) or by cooperating in the use of the substrates. In a microbial community, cooperation is more important because of functional specialization. Knowledge of the functions of microorganisms makes it possible to construct trophic coupling schemes based on product-substrate interactions between forms, for concentration of the given metabolites, which make it possible to regulate the physical and physical-chemical properties of CMs: to improve plasticity of the mix and the pouring properties of slip, change the color, remove undesirable iron impurities, calcium carbonates, and so on.

**Microstructure and Mineral Composition of CMs after Aging.** During the aging period (mainly under the influence of gleying) the macro- and microstructure, granulometric, and material compositions, transformation and synthesis of new minerals occur in CMs.

During gley-genesis, at least three processes occur simultaneously as a result of the vital activity of microorganisms:

transformation of the phase contacts of the cemented particles and microaggregates of the CMs in coagulation contact;

dispersing of particles and destruction of their crystal structure; and,

synthesis of new minerals, for example biogenic magnetite and iron sulfide.

In [20] the assumption of cementing action of shells consisting of aluminosilica is presented on the bases of a hypothesis about the nature of the lack of plasticity in refractory clays. It was shown that colloids cannot be separated from nonplastic clays by simple elutriation. In accordance with the classification of the biochemical processes [8] the cemented phase contacts actively develop at the rubefaction stage during a period of dehydration of the CMs. To change the rheological properties of nonplastic clays it is necessary, first and foremost, to destroy the initial macro- and microstructure of the CM. Ordinarily, finely dispersed chemogenic calcite, iron oxides and hydroxides, amorphous silica, organic matter, and other substances serve as the cementing phase. During gley-genesis, in the course of metabolism microorganisms release into the medium various metabolites-products which are strong chemical reagents: mineral and organic acids, biogenic alkali, chelate formers, and substances possessing strong reducing and surfactant properties. In summary, microorganisms are capable of indirectly acting on the strength of the phase contacts of a crystallization or cementation nature, transforming them into coagulation contacts.

A new macro- and microstructure with elevated density and low intra-aggregate porosity forms in CMs as a result of gley formation and subsequent drying. The main change of the density and pore space is due to the decrease in the number of the largest pores, destruction of the cementation phase, peptization of the macro- and microaggregates, dispersing of the surface particles of the minerals, formation of colloids and their settling in pores.

It is shown in [4] they gley-genesis affects the mineral composition and micromorphology of surface particles of kaolin and porcelain stone: with the kaolinite structure preserved the degree of crystallinity of the kaolinite decreases as a result of surface amorphization; part of the crystals of kaolinite, muscovite, and an unstable calcium compound is destroyed; soluble iron compounds form as a result of the reaction  $\text{Fe(III)} \rightarrow \text{Fe(II)}$ .

Several hypotheses have been advanced concerning the mechanism of degradation of layered silicates under the influence of gleying [2]. This process should occur especially intensely in a stagnant-laving regime, since such conditions make it possible for the products of decomposition to be removed from the reaction zone.

During aging of CMs, after gley-genesis and subsequently during drying the coagulation contacts transform into condensation contacts, substances are transferred through pores and settle on particle of the dispersed phase, predominately clayey particles, right up to the appearance condensation-crystallization contacts with an intermediate finely dispersed phase — a solid solution, which, in the first place, binds individual particles more strongly by means of phase contacts — bridges — and, in the second place, is in a more active state for subsequent recrystallization, i.e., it forms activations centers for the process.

**Identification of Gley Processes.** The following can be used to identify the biochemical processes during aging of CMs and determining the optimal aging time:

color characteristics of the samples of CM mixes in different aging periods;

criteria for assessing the oxidation-reduction state of the CM medium; and,

chemical criteria for gleying, which are based on the ratio of the different forms of iron compounds.

**Color Characteristics.** Clayey materials are determined in the coordinate spaces  $L^* a^* b^*$  two axes of which characterize the chromaticity:  $a^*$  axis — degree of redness ( $+a^*$ ) and greenness ( $-a^*$ );  $b^*$  axis — degree of yellowness ( $+b^*$ ) and blueness ( $-b^*$ ). The third axis, which is perpendicular to the chromaticity plane ( $a^* - b^*$ ), determines the color brightness  $L^*$  (from 0 to 100).

During the aging of CMs, as gley-genesis progresses, the brightness indicator  $L^*$  decreases in direct proportion to the color saturation, the chromaticity coordinates shift from the red-yellow region in the region corresponding to blue-green. This change is due to, first and foremost, the reduction  $\text{Fe(III)} \rightarrow \text{Fe(II)}$ . A red-yellow color of the initial CM indicates the presence of iron hydroxides, mainly hematite and

goethite, respectively; this is confirmed by electron paramagnetic resonance studies and Mössbauer spectroscopy; the blue-green color of CMs, right up to a grey-black color, is due to Fe(II) as well as colloidal iron sulfate and biogenic magnetite particles, which are black.

A light-blue or green color in certain gleyed mixes of CMs is unstable; it changes under oxidative conditions, for example during drying of these masses, from white-grey to yellow-red depending on the iron content. It is shown in [2, 8] that green color becomes stable after gleying of CMs provided that montmorillonite or smectite is present in them.

#### **Criteria for Assessing the Oxidation-Reduction State.**

Currently, CM media in an aging state are divided into two large groups according to whether oxidizing or reducing conditions predominate. The magnitude and dynamics of the oxidation-reduction state of a CM medium depends, first and foremost, on the hydrothermal regime of the process. The moisture content determines the aeration of the CMs and, in combination with the temperature regime, the intensity and direction of development of the biocenoses and biochemical processes. If the CM medium, waterlogged for a short time, compensates the consequences of short-time anaerobiosis, a reducing medium does not become predominant. In this connection, for sufficiently high degree of prolonged waterlogging the change of the oxidation-reduction state in the direction of a reduction of oxygen stores in CMs becomes stable, making possible anaerobic biocenosis and reducing conditions to predominate. When organic and mineral components are present in CMs anaerobiosis promotes the formation of new chemical and biochemical systems in the direction of development of gley-genesis.

The following indicators can be used as criteria to evaluate the oxidation-reduction state of the CM medium and determine the optimal storage time: the redox potential expressed in millivolts, the computed value of the redox potential, and the combined redox potential.

**Redox Potential Eh Expressed in Millivolts.** The flow of some redox reactions or others is characterized by a definite range of *Eh*. Ordinarily, depending on the conditions the values of *Eh* for different CMs lie in the range 100 – 750 mV, sometimes decreasing to negative values. To a first approximation the following ranking can be used: a decrease of *Eh* to 350 – 450 mV indicates that a medium in which reducing conditions replace oxidative conditions. An ORP of the order of 20 mV and less attests to intense development in the CM of reducing conditions, development of anaerobic processes, and formation of Fe(II) with the typical indications of gley formation.

**Computed Value of the Redox Potential Eh**, expressed in terms of the electron activity *pe* can be determined from Nernst's equation [8]:

$$pe = Eh : 58,$$

where *Eh* is expressed in mV.

The calculation was performed at 25°C.

The grading of the values of the redox potential, expressed in terms of the electron activity *pe* according to G. L. Spozito [21] is presented in the form of the following sequence for pH = 7:

CM state:

oxidized . . . . .	+ 7.0 < <i>pe</i> < + 13.5
moderately reduced . . . . .	+ 2.0 < <i>pe</i> < + 7.0
reduced . . . . .	- 2.0 < <i>pe</i> < + 2.0
strongly reduced . . . . .	- 6.8 < <i>pe</i> < - 2.0

*Combined redox potential gH*, which takes account of proton activity (pH) as well as electron activity (*pe*), to evaluate the oxidation-reduction conditions in the medium:

$$gH = 2(pe + pH).$$

The sum (*pe* + pH) is used as an equilibrium constant for a half-reaction, related with the transfer of an electron and a proton. It has been suggested that it be named as the redox parameter that characterizes the sum of all oxidation-reduction constants [22]. If *gH* > 27, oxidizing processes predominate and if *gH* < 27, then reducing processes predominate. If *gH* < 20, intense development of reducing processes (gleying process) occurs.

The main chemical elements participating redox reactions in a CM medium are C, Fe, Mn, N, O, and S. A definite sequence in the reduction of these elements has been found theoretically. The calculation of the activity of electrons in the reduction of different elements makes it possible to obtain critical values *pe*<sub>crit</sub> [21]. For pH = 7 O<sub>2</sub> is reduced to H<sub>2</sub>O first (*pe*<sub>crit</sub> = 5.4), then Fe(OH)<sub>3</sub> to Fe<sup>2+</sup> (*pe*<sub>crit</sub> = 1.9) and, finally, SO<sup>2-</sup> to S<sup>2+</sup> (*pe*<sub>crit</sub> = - 5.3).

**Chemical Criteria for Gleying.** During gleying of CMs, the content of amorphous and organomineral iron, extracted by means of Tamm extraction [8], increases. This is due to the transition of iron hydroxide from the crystallized into the amorphous state, an increase of the Fe<sup>2+</sup> concentration in the liquid phase and the migration of Fe<sup>2+</sup> ions into the surface layers, their oxidation and precipitation in the form of hydroxides.

The Shvertman ratio Fe<sub>ox</sub>/Fe<sub>dit</sub> is the ratio of the oxalate dissolved iron according to Tamm (it determines Fe<sub>ox</sub> and is interpreted as the amount of iron in amorphous or weakly crystallized iron oxides Fe<sub>ox</sub> = Fe<sub>am</sub>) to the dithionite-dissolved iron according to the Mehr – Jackson method, which permits determining Fe<sub>dit</sub> and is interpreted as the amount of iron in free or nonsilicate compounds (Fe<sub>dit</sub> = Fe<sub>free</sub>). The Svertman ratio is used to evaluate the manifestation of the gleying process: if the ratio is greater than 0.3, then it can be assumed that gleying of CM is present.

**Properties of CMs after Aging and Ceramic Samples Based on Them.** As a result of gleying of CMs during aging their chemical and physical-chemical properties change as follows [4, 5, 15, 16]:

the pH decreases and the main substances cementing aggregates are removed (the content of potassium, sodium,

iron, calcium, and especially silicon cations in the filtrate of water extracts increases);

the content of total and dissolved iron in the water extract increases;

the filtration power of CM suspension decreases;

the optimal moisture content for molding, due to the low values of the moisture content and yield stress, decreases with equal plastic strength and interval of the plastic state;

for the same moisture content in the slip and equal concentration of electrolyte, the Engler flowability increases and the thickening constant decreases;

the buildup rate of thickness and mass of a casting increases with the same moisture content, which attests to adequate moisture transfer to the experimental paste;

the linear shrinkage in air decreases;

the values of the apparent density and ultimate strength under bending of air-dry samples increase;

sintering of the experimental samples of CMs as compared with control samples is more intense, the interval of the sintered state shifts to lower temperatures and expands during sintering;

after CMs are sintered the true and apparent density, the ultimate strength under static bending and impact of the ceramic samples increase;

the degree of "ripening" and homogenization of the heterophase matrix of the ceramic samples increases: quartz dissolves more rapidly, the amount of glass phase increases, the ratio of the content of the primary flaky and secondary needle-shaped secondary mullite increases in the direction of larger amounts of mullite.

So, it can be stated that the gley formation processes affect the formation of the coagulation structure of the matrix, on whose basis subsequent types of structures right up to the condensation-crystallization structure of a semi-finished article are formed, and sintering of CMs intensifies [23].

Analysis of the information presented above makes it possible to evaluate a number of the most important biochemical processes, including the most important one — gley formation, which occur during aging of CMs, and their effect on the physical-mechanical properties of ceramic.

Setting the direction of biochemical processes artificially so as to develop gleying creates the possibility of regulating the macro- and microstructures and technological properties of CMs by means of bioactivation of coagulation structure-formation in water dispersions.

The direction and intensity of biochemical processes will be determined by the number of necessary and sufficient factors: moisture content, water regime, content and composition of the organic matter, presence of natural microflora, temperature-time regime of the aging of CMs.

To identify biochemical processes and determine the optimal aging time of CMs it is proposed that a comprehensive assessment be made using color characteristics, the oxidation-reduction state of the medium, and chemical criteria based on the ratio of the forms of iron compounds.

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